

# Surfactant Mixtures for Control of Bubble Surface Mobility in Foam Studies

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A new class of surfactant mixtures is described, which is particularly suitable for studies related to foam dynamics, such as studies of foam rheology, liquid drainage from foams and foam films, and bubble coarsening and rearrangement. These mixtures contain an anionic surfactant, a zwitterionic surfactant, and fatty acids (e.g., myristic or lauric) of low concentration. Solutions of these surfactant mixtures exhibit Newtonian behavior, and their viscosity could be varied by using glycerol. Most importantly, the dynamic surface properties of these solutions, such as their surface dilatational modulus, strongly depend on the presence and on the chain-length of fatty acid(s). Illustrative results are shown to demonstrate the dependence of solution properties on the composition of the surfactant mixture, and the resulting effects on foam rheological properties, foam film drainage, and bubble Ostwald ripening. The observed high surface modulus in the presence of fatty acids is explained with the formation of a surface condensed phase of fatty acid molecules in the surfactant adsorption layer.

## 1. Introduction

During the past 10 years, dynamic processes in foams (foam flow, liquid drainage, bubble coarsening and rearrangement, etc.) have attracted considerable attention from researchers,<sup>1–25</sup> because of the practical importance of these processes and, yet, their poor scientific understanding. It was clearly demonstrated by experiments that foam dynamic properties depend not only on mean bubble size, bubble polydispersity, air volume fraction,

and equilibrium surface tension (the four most important characteristics governing the properties of static foams), but also on the dynamic properties of the surfactant adsorption layers, such as surface modulus, surface viscosity, characteristic adsorption time, and so forth.<sup>1–6,8–13,18–20,22,24,25</sup>

Despite the recognized importance of the dynamic surface properties, the specific properties that are decisive for one phenomenon or another in foam dynamics are still rather obscure. Therefore, the role of surfactants in these studies is discussed by using different terms, such as “surface rigidity”,<sup>1–3,8</sup> “surface tangential mobility”,<sup>1–3</sup> “surface viscosity”,<sup>5,7–10</sup> or “surface elasticity”,<sup>6</sup> often associated with the “Marangoni effect”,<sup>4</sup> which are often considered as just convenient phenomenological parameters reflecting different surface properties, without explicit account of the actual surface dynamics. For many of the foam-related phenomena, it is far from clear both experimentally and theoretically how one should describe the bubble surface properties and how these properties could be incorporated in the theoretical description of macroscopic foam behavior.

One of the main difficulties in these studies is the lack of appropriate model surfactants, covering a wide range of surface properties, which would allow one to perform systematic characterization of the role of these properties in foam dynamics. Until now, the preferred stabilizers used for modifying the bubble surface properties have been (1) proteins,<sup>3,18</sup> (2) lauryl alcohol (LA) as a cosurfactant to sodium dodecyl sulfate (SDS) or dodecyl trimethyl ammonium bromide (DTAB),<sup>1,7–10,22</sup> and (3) sodium or potassium salts of fatty acids.<sup>19,20</sup>

The main problem with proteins is that the properties of their adsorption layers gradually change with time,<sup>26–28</sup> which creates significant difficulties in performing the experiments and in the subsequent data analysis. Also, the properties of different batch samples of the same protein could vary, as a result of subtle

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details in sample preparation and storage, which results in low reproducibility and difficulties in the comparison of results obtained by different research groups. Furthermore, the protein-stabilized foams are prone to bubble–bubble coalescence, and for all these reasons, proteins are not very suitable for systematic studies of foam dynamics.

Mixtures of SDS+LA and DTAB+LA were successfully used to demonstrate the effect of surface tangential mobility for liquid drainage from foams and foam films, and through Plateau borders.<sup>1,7–10,22</sup> However, these systems also have disadvantages, which create experimental problems. The most important of them are (1) LA significantly affects the surface properties only if it is taken above its solubility limit, so that the foaming solutions contain droplets of LA, nonsolubilized in the surfactant micelles, and (2) it has not been shown so far whether a sufficiently wide range and systematic variation of the surface properties could be achieved with these systems. In other words, the LA-containing solutions with relatively high surface modulus are nonhomogeneous (the foam is a three-phase system), and no possibility for systematic variation of their properties has been demonstrated.

The sodium and potassium salts of fatty acids (called also “soaps”) have the important advantage that their surface properties could be varied in a relatively wide range, by changing the chain-length of the surfactant molecules and pH of the solutions. The main problem with these solutions is that they contain insoluble surfactant precipitates in the form of crystallites with complex composition.<sup>19,29</sup> To remove these precipitates, the original turbid surfactant solutions should be centrifuged and filtered just before foam generation and the subsequent foam experiments. However, the surfactant precipitates spontaneously reappear in the foaming solutions, typically within ~5–10 min after filtering, at room temperature. Therefore, the foam experiments should be relatively fast, if the study is to be completed in the absence of precipitates, which could jeopardize the experiment. In addition, the sodium salts of fatty acids often precipitate in the form of fibrous crystallites, which lead to non-Newtonian behavior of the surfactant solution.

In conclusion, neither of the systems used so far satisfies all basic requirements, which would allow systematic study of the role of bubble surface properties in foam dynamics, namely, (1) a wide range of surface moduli that are reproducible and stable with time, and (2) Newtonian behavior of clear foaming solution (without precipitates), with the possibility for variation of solution's bulk viscosity.

## 2. Composition of the Proposed Surfactant Mixtures

In the current letter we suggest an alternative foaming system, which seems to address all issues mentioned above and, from this viewpoint, seems particularly suitable for studies of foam dynamics. The system presents a mixture of an anionic surfactant sodium lauryl-dioxyethylene sulfate (SLES), zwitterionic surfactant cocoamidopropyl betaine (CAPB), and medium-chain fatty acids, which could be with different numbers of carbon atoms. In the current study we used fatty acids with 12 and 14 carbon atoms, i.e., lauric acid (LAc) and myristic acid (MAc), but other fatty acids and their mixtures could be also used to tune the solution surface properties.

The role of each component in this mixture is as follows:

The *anionic surfactant SLES* gives rather mobile bubble surfaces (low surface modulus, and negligible surface elasticity and viscosity at low frequencies of surface oscillations), due to

relatively fast exchange of the SLES molecules between the surface and the underlying liquid phase.

The *zwitterionic surfactant CAPB* improves foam stability without significantly changing the solution surface modulus (at low frequency) and foam rheological properties. In addition, CAPB improves the solubilization capacity of the SLES micelles with respect to the fatty acids, thus allowing one to vary the composition and the surface properties of the foaming solutions in wider range. CAPB may increase the surface modulus at high frequencies of oscillations (compared to solutions containing SLES only), but we could not prove or reject this possibility with the available experimental techniques.

The *fatty acids* are a key component in the mixture because, depending on their concentration and chain-length and on temperature, they can induce very high surface dilatational modulus (even at low frequency of surface oscillations), which leads to tangentially immobile bubble surfaces in dynamic experiments (see Section 3 below for results demonstrating this effect). Note that mixed micelles of SLES+CAPB are needed to solubilize the fatty acids up to sufficiently high concentrations in the surfactant solution; otherwise, the fatty acids remain in the form of insoluble precipitates and are not convenient for foam studies.

Other anionic surfactants, such as SDS, also provide low surface modulus and can solubilize fatty acids. However, we found experimentally that SDS+LAc solutions also exhibit rather low surface modulus at room temperature (with and without CAPB). Therefore, further studies are planned to check whether SDS-based solutions can be formulated to provide high surface modulus (similar to those observed with SLES), thus allowing one to formulate SDS-containing mixtures with tuneable surface properties.

The results shown below are obtained with the following chemicals: SLES (product of Stepan Co., Northfield, IL; commercial name STEOL CS-170), CAPB (product of Goldschmidt, Essen, Germany; commercial name Tego Betaine F50), LAc (product of Acros Organics, Geel, Belgium; 99.5+ %, Cat. No. 16728-5000), SDS (Acros Organics; > 98.5% GC, Cat. No. 23042-5000), MAc (Fluka, Buchs, Switzerland; purum ≥98.0 GC, Cat. No. 70082), and Glycerol (Fluka, anhydrous p.a. ≥ 99.5% GC, Cat. No. 49770). All chemicals were used as received, without additional purification.

The foaming solutions were prepared as follows: First, we prepared stock solution with total surfactant concentration of 10 wt % (6.6 wt % SLES + 3.4 wt % CAPB). Next, we dissolved 0.4 wt % of LAc or MAc in this concentrated solution, by heating the mixture in water bath at 50 °C (for LAc) or 60 °C (for MAc), under mild stirring, until a clear solution was formed. After cooling this solution to room temperature, the obtained concentrated solutions were diluted 20 times with deionized water from Milli-Q (Millipore). In this way, we prepared the final foaming solutions, which contained 0.33 wt % SLES and 0.17 wt % CAPB, with or without 0.02 wt % LAc or MAc (for foam experiments at high bubble volume fraction ( $\Phi > 0.90$ ) and small mean bubble radius ( $R_{32} < 200 \mu\text{m}$ ), solutions containing 0.05 wt % of LAc or MAc are recommended to avoid the possible depletion of the solution, as a result of LAc/MAc adsorption on bubble surface).

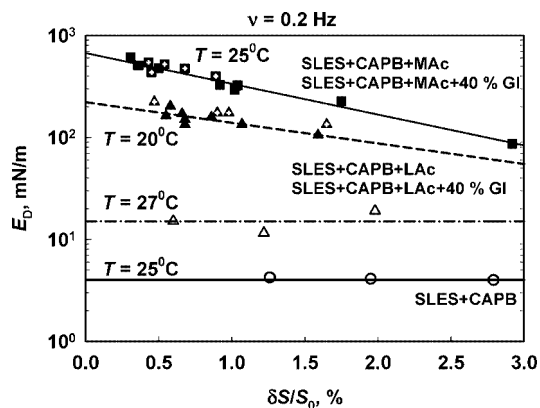
The pH of all these solutions was around 6.5. The recommended temperature range for the experiments with the LAc-containing solutions is 18 to 22 °C, whereas for MAc-containing solutions it is 20–27 °C. The reason for specifying such relatively narrow temperature ranges is that precipitates of fatty acids could be formed at lower temperatures, whereas the surface modulus decreases very sharply at higher temperatures (>25 °C for LAc and >30 °C for MAc) for reasons explained in Section 4 below.

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Table 1. Properties of the Studied Surfactant Solutions<sup>a</sup>

system	glycerol	$T$ , °C	$\mu$ , mPa·s	$\sigma$ , mN/m	surface modulus <sup>b</sup>			power-law index for foam–wall friction, $m$	power-law index for friction inside foam, $n$
					$E_{DS}$ , mN/m	$E_{DL}$ , mN/m	$E_D$ , mN/m		
SLES+betaine	0	25	0.9	28.5	3.4	2.5	4.2	$2/3 \pm 0.01$	0.47
		40	3.80						0.42
	60	25	3.28	28.9	4.7	2.6	5.4	0.42	
		30	2.83					0.43	
SLES+betaine+LAc	0	25	9.35	29.2				$1/2 \pm 0.03$	0.40
		40	1.01	23.8	60	130	143		0.24
	60	27	-	25.4	11	10	15	$1/2 \pm 0.03$	0.31
		30	3.76	23.9				$2/3 \pm 0.01$	0.40
SLES+betaine+MAc	0	25	2.90	25.8				$1/2 \pm 0.03$	0.30
		40	10.9	23.6					0.22
	60	25	0.91	23.8	110	285	305	$1/2 \pm 0.03$	0.42
		30	0.83					0.28	
SLES+betaine+LAc	0	25	3.33	23.3	200	330	360	$1/2 \pm 0.03$	0.36
		40	2.85	24.5					0.33
	60	25	9.29	23.1				0.33	
		30	7.62					0.36	

<sup>a</sup>  $\mu$  is viscosity of bulk solutions,  $\sigma$  is surface tension,  $E_{DS}$  is storage (elastic) surface dilatational modulus,  $E_{DL}$  is loss (viscous) surface dilatational modulus,  $E_D = (E_{DS}^2 + E_{DL}^2)^{1/2}$  is the total surface dilatational modulus,  $m$  is power-law index for foam–wall friction,  $n$  is power-law index for inside-foam friction (see ref 19 for definitions of  $n$  and  $m$ ). The surface dilatational moduli are measured by the oscillating drop method on a DSA10 instrument equipped with an ODM/EDM module (Kruess, Germany). The foam rheological properties are determined with foams having air-volume fraction,  $\Phi = 0.90$ , by the methods described in ref 19 on a Bohlin Gemini rheometer (Malvern Instruments, U.K.). <sup>b</sup> Data for  $\nu = 0.2$  Hz and  $\delta S/S_0 = 1\%$ .



**Figure 1.** Total surface dilatational modulus,  $E_D$ , of several surfactant solutions, as a function of the relative surface deformation, measured by drop-shape analysis (DSA) of oscillating pendant drops (5 s oscillation period and different temperatures as shown in the figure). The measurements are performed on a DSA10 instrument, equipped with an ODM/EDM module (Kruess, Germany). Symbols denote SLES+CAPB at 25 °C (open circles); SLES+CAPB+LAc at 27 °C (open triangles); SLES+CAPB+LAc at 20 °C (filled triangles); SLES+CAPB+LAc+40 wt % glycerol at 20 °C (crossed triangles); SLES+CAPB+MAc at 25 °C (filled squares); SLES+CAPB+MAc+40 wt % glycerol at 25 °C (crossed squares).

In the recommended range of temperatures, all solutions are clear, with viscosity practically equal to that of water, and surface dilatational modulus  $E_d \approx 300$  mN/m for MAc at 25 °C and  $E_d \approx 150$  mN/m for LAc at 20 °C (both measured by the oscillating drop method at a frequency of 0.2 Hz and an amplitude of 1%). For comparison, the surface elastic modulus of the SLES+CAPB solution without fatty acids is  $E_d \approx 4$  mN/m (see Table 1 and Figure 1).

Although SLES and CAPB are not pure individual surfactants, we found that the main properties of the recommended solutions do not depend significantly on the specific surfactant batch, and, after measuring the solution surface tension (and surface elasticity and viscosity, if their exact values are needed for data interpretation), one can conveniently use these commercial surfactants for dynamic foam studies. In some of the foam experiments, as shown in ref 19 and in Figure 2A below, one needs only qualitative information about the surface properties, e.g., “high” or “low”

surface modulus (which corresponds to tangentially mobile or immobile bubble surfaces, respectively). Such qualitatively different systems are easily prepared by using SLES+CAPB mixture (for mobile surface) and SLES+CAPB+LAc or SLES+CAPB+MAc mixture at an appropriate temperature (for an immobile surface; see Figure 1 and Table 1).

### 3. Illustrative Results

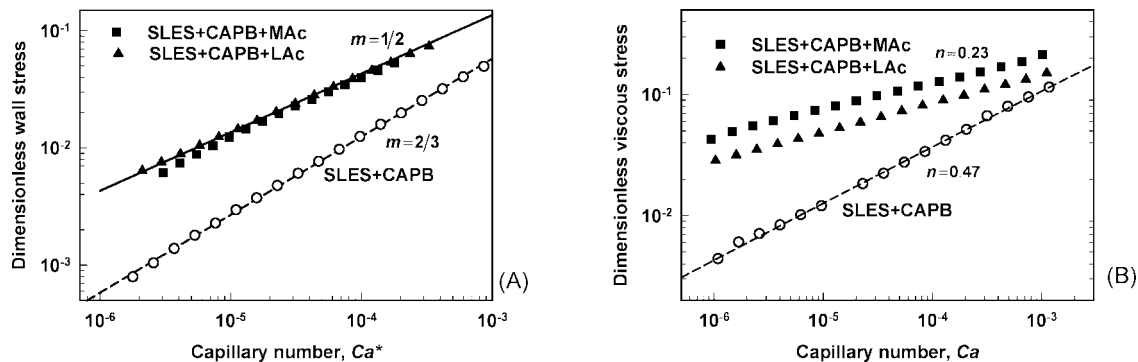
In this section we demonstrate how several dynamic properties of foams are affected by the addition of MAc or LAc to the SLES+CAPB surfactant mixture. First we show and discuss the viscous friction between a foam and a moving solid wall (foam–wall friction), and between bubbles inside a sheared foam. These data are obtained by parallel-plate rheometry as described in ref 19 on a Bohlin Gemini instrument (Malvern Instruments, U.K.). The mean volume–surface bubble radius,  $R_{32}$ , used for scaling of the rheological data and for characterizing the rate of Ostwald ripening, was determined by the method described in ref 19 after measuring the size of at least 800 bubbles for each sample studied.

In previous studies<sup>19,20,30,31</sup> we showed theoretically and experimentally that the surface mobility of the bubbles has a strong impact on foam rheology in two main aspects. First, the viscous stress is much higher in magnitude for immobile surfaces, as compared to mobile surfaces. Second, the numerical indexes, characterizing the power-law dependence of the viscous stress, as a function of the respective capillary number ( $Ca$  for inside-foam friction or  $Ca^*$  for foam–wall friction; see below for definitions), are different for tangentially mobile and immobile surfaces. Thus, for foam–wall friction, the power-law index is  $m = 2/3$  for mobile surfaces and  $m = 1/2$  for immobile surfaces.<sup>19,20</sup> For inside-foam friction, the power-law index is  $n \approx 0.25$  for bubbles with high surface modulus and  $n \approx 1/2$  for bubbles with low surface modulus.<sup>19,30,31</sup> The effect of surface dilatational modulus on inside-foam friction was explained in ref 31 with the fact that the bubbles in a steadily sheared foam perpetually change their surface area around some mean value,

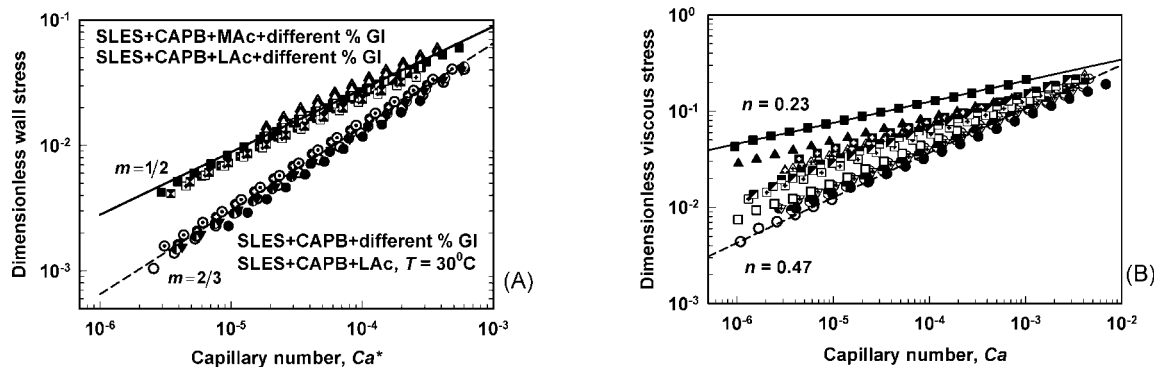
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**Figure 2.** Illustrative results for the effect of MAc and LAc on foam rheological properties. (A) Dimensionless foam–wall viscous stress,  $\tau_w/(\sigma/R_{32})$  as a function of capillary number,  $Ca^* = \mu V_0/\sigma$ ; (B) dimensionless inside-foam viscous stress,  $\tau_v/(\sigma/R_{32})$  as a function of the foam capillary number,  $Ca = \mu \dot{\gamma} R_{32}/\sigma$ . The foams are prepared from solutions of SLES+CAPB (open circles), SLES+CAPB+LAc (filled triangles), or SLES+CAPB+MAc (filled squares). The lines are drawn as eye-guides with slopes corresponding to the indicated flow indexes,  $n$  and  $m$ . The dashed line in (B) is a theoretical prediction, eq 48 in ref 31 at air volume fraction  $\Phi = 0.90$ .



**Figure 3.** Results demonstrating the scaling of foam rheological data for different bulk viscosities and surface moduli of the foaming solutions (see also Table 1). (A) Dimensionless foam–wall viscous stress,  $\tau_w/(\sigma/R_{32})$  as a function of capillary number,  $Ca^* = \mu V_0/\sigma$ ; (B) dimensionless inside-foam viscous stress,  $\tau_v/(\sigma/R_{32})$  as a function of foam capillary number,  $Ca = \mu \dot{\gamma} R_{32}/\sigma$ . Air volume fraction is  $\Phi = 0.90$ . Viscosity was changed by using glycerol (GI) of concentration varied between 0 and 60 wt %, which corresponds to viscosity variation from ca. 1 mPa·s to 10 mPa·s. The lines are drawn as eye-guides with slopes corresponding to the indicated flow indexes,  $n$  and  $m$ . The dashed line in (B) is a theoretical prediction (eq 48 in ref 31).

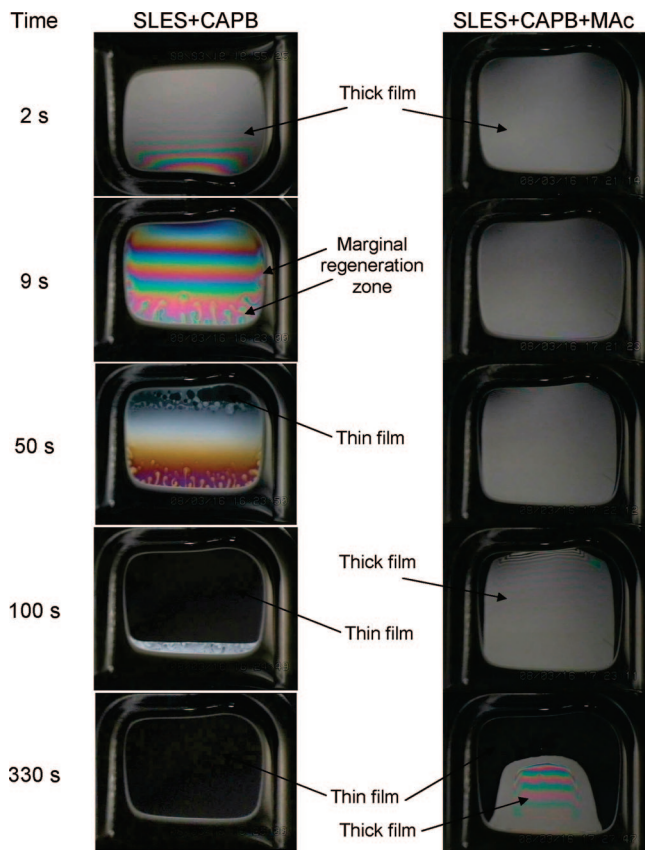
as a result of collisions with the neighboring bubbles and the related formation of transient foam films. This variation of the bubble area leads to energy dissipation on the bubble surface, which is directly proportional to the surface dilatational loss modulus,  $E_{DL}$ .

Measurements of rheological properties of foams, prepared from the surfactant mixtures described in Section 2, clearly demonstrated the significant effect of MAc and LAc on the surface mobility of the bubbles. As illustrations, we show the effect of MAc on the measured viscous stress for foam–wall friction in Figure 2A and for inside-foam friction in Figure 2B. As seen from these figures, the increased surface modulus after the addition of MAc to the surfactant mixture (see Table 1) leads to changes in the power-law indexes in line with the theoretical predictions and with previous experimental results: from  $m = 2/3$  to  $m = 1/2$  for foam–wall friction and from  $n \approx 1/2$  to  $n \approx 0.25$  for inside-foam friction. For both types of experiments, the viscous stress is much higher in the presence of MAc, as predicted theoretically.<sup>19,20,31</sup>

Similar results are obtained in the presence of LAc, with the main difference being the lower viscous friction inside the LAc-containing foams (compared to MAc), which is certainly related to the lower surface modulus (and lower surface viscosity) of the respective solution<sup>31</sup> (cf. Figure 1 with Figure 2B). The quantitative analysis of the effect of surface properties on the inside-foam viscous stress requires considerable theoretical efforts and is under investigation now.

It is important to note that the bulk viscosity of the studied solutions can be varied from  $\sim 1$  mPa·s up to ca. 10 mPa·s by adding up to 60 wt % of glycerol, without changing very significantly the solutions' surface properties. This statement is illustrated with the data shown in Figure 3A, where the results for foam–wall friction stress, obtained with solutions containing different concentrations of glycerol, are shown as dimensionless viscous stress,  $\tau_w/(\sigma/R_{32})$ , vs dimensionless capillary number,  $Ca^* = \mu V_0/\sigma$  (here,  $\mu$  is solution viscosity,  $V_0$  is velocity of the moving wall,  $\sigma$  is surface tension, and  $R_{32}$  is the mean volume–surface radius of the bubbles). Note that the results for the various solutions, shown in Figure 3A, merge into two master lines, one of them with  $m \approx 2/3$  for mobile surfaces (with all solutions exhibiting low surface modulus) and another one with  $m \approx 1/2$  for immobile surfaces (with all solutions exhibiting high surface modulus). These master lines demonstrate the proper scaling of all experimental data with the bulk viscosity of the solutions.<sup>19</sup>

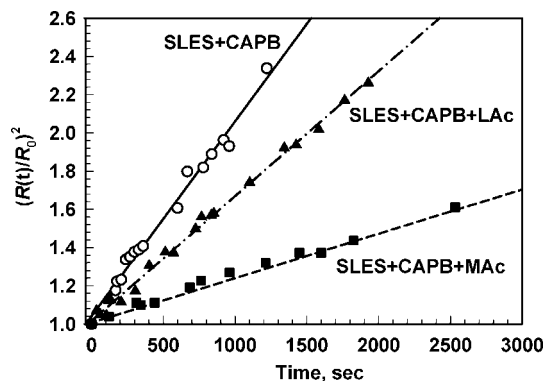
As expected, all results for inside-foam viscous friction, obtained with solutions exhibiting low surface modulus, scale well with the capillary number characterizing foam friction,  $Ca = \mu \dot{\gamma} R_{32}/\sigma$  (see the data falling on the master line with slope  $n = 0.47$  in Figures 2B and 3B).<sup>30</sup> On the other hand, the results, obtained with solutions containing MAc or LAc and exhibiting high surface moduli, do not fall on this master line. The latter nontrivial result is explained in ref 31 by the fact that the viscous stress in these “high-modulus” systems contains two components,



**Figure 4.** Images of thinning foam films, formed by rapid withdrawal of a rectangular glass frame ( $6 \times 4 \text{ mm}^2$ ) from surfactant solution and observed in polychromatic light: foam film from SLES+CAPB solution (left column of images); foam film from SLES+CAPB+MAc solution (right column of images).

which scale rather differently with  $\text{Ca}$ . The first component is created by the viscous friction inside the foam films between neighboring bubbles and is approximately proportional to  $\text{Ca}^{1/2}$ , whereas the second component is created by the energy dissipated on the bubble surface and does not scale with the capillary number. Because the second component is proportional to the surface loss modulus of the bubbles  $E_{\text{DL}}$  (which is different for the various systems), its contribution is different for the various “high-modulus” systems shown in Figure 3B, and no merging of all data around a single master line is possible. According to the analysis in ref 31, this second component is significant if the surface loss modulus of the solutions is relatively high,  $E_s > 20 \text{ mPa} \cdot \text{s}$ , which is the case with the fatty acid-containing solutions. For all systems exhibiting low surface modulus, the component related to surface dissipation is negligible, and the data pack around the master line with  $n = 0.47$ , characterizing the friction in foam films only.

The importance of surface properties is further illustrated with the mode and rate of drainage of vertical foam films, formed by withdrawal of a rectangular glass frame from the surfactant solution.<sup>22,32,33</sup> As seen from the image panel in Figure 4 (left column), the films formed from SLES+CAPB solution thin with a well-pronounced marginal regeneration zone at the film periphery and in the lower zone of the film (close to the solution surface). The process of film thinning is completed within  $\sim 100 \text{ s}$ , with the formation of very thin (appearing black in reflected



**Figure 5.** Change of mean bubble radius,  $R_{32}$ , with time, as a result of Ostwald ripening (molecular gas transfer from smaller to larger bubbles). The line slope is inversely proportional to the characteristic time of the Ostwald ripening process. The bubbles are observed at the foam contact with a glass plate (only the size of the first layer of bubbles was measured).

light) equilibrium foam film. This is a typical thinning pattern for foam films formed from solutions of synthetic surfactants with low surface modulus. In contrast, no marginal regeneration zone is seen in the films containing MAc (right column of images in Figure 4), and, as a result, the mode of film thinning is rather different and the process is much slower: the black film occupies the entire film area after  $\sim 500 \text{ s}$ .

Another series of experiments demonstrated that the rate of bubble Ostwald ripening is also substantially reduced in the presence of MAc and (to a lesser extent) by LAc. For the SLES+CAPB system, exhibiting very fast relaxation of the surface tension upon surface expansion or contraction, it is known that the rate-determining step in the Ostwald ripening process is the molecular dissolution and diffusion of gas across the aqueous films separating the bubbles.<sup>11,12,34–37</sup> Because LAc and MAc are not expected to noticeably change the air solubility in water, and because the foam films were found to have similar equilibrium thickness in all three systems, the main effect of MAc and LAc on Ostwald ripening should be explained by the different surface properties of the solutions.

One possible explanation is that the gas permeability of the adsorption layers is reduced<sup>34,35</sup> in the presence of LAc and MAc. Another, very probable explanation of the reduced rate of Ostwald ripening in these systems could be the slower desorption time of the surfactant molecules from the surfaces of the MAc and LAc-containing solutions. Indeed, step-relaxation experiments by the pendant drop method showed that the relaxation of surface tension to its equilibrium value, after a small stepwise decrease of the drop area by 2%, could be described well by exponential function, with characteristic relaxation time,  $t_R \ll 1 \text{ s}$  for SLES+CAPB solution,  $4 \pm 1 \text{ s}$  for LAc-containing solution, and  $10 \pm 2 \text{ s}$  for MAc-containing solution. Note that the ratio of the relaxation times for the MAc and LAc solutions is  $2.5 \pm 0.5$ , and is very similar to the ratio of the slopes of the lines characterizing the rate of Ostwald ripening,  $2.8 \pm 0.3$  (see Figure 5). Similar explanation could be given to the complete

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arrest of Ostwald ripening by solid particles, which is still a matter of debate in the literature.<sup>38–40</sup> Because of the very high desorption energy of the solid particles, their characteristic desorption time is infinitely long (in the practical time-scale) and the Ostwald ripening is stopped.

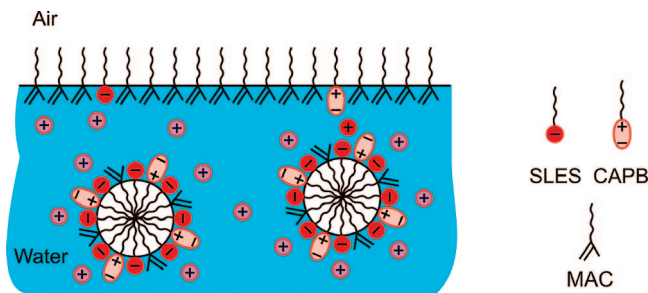
With respect to Ostwald ripening, the protein molecules have intermediate properties between the typical low-molecular mass surfactants (such as SLES and CAPB) and the solid particles: the proteins significantly decelerate this process without completely arresting it.<sup>41</sup> This result could also be explained with the relatively slow desorption of the protein molecules from compressed adsorption layers,<sup>42</sup> like those forming on the surfaces of shrinking bubbles in coarsening foam. Currently, we perform systematic experiments with various systems, aimed to clarify unambiguously which surface properties of the bubbles are governing Ostwald ripening in foams.

#### 4. Molecular Origin of the High Surface Modulus in the Systems Studied

Hints for the molecular origin of the high surface modulus in the systems containing fatty acids are provided by several experimental facts. First, the surface tension and the surface moduli of the solutions containing fatty acids (beside SLES and CAPB) are very similar to those measured with the solutions of the individual fatty acids and are very different from those measured with solutions of SLES and CAPB (without fatty acids). This observation indicates that the adsorption layers in the mixed solutions are strongly enriched in fatty acid molecules (MAc and LAc), which dominate the surface properties of these solutions. Second, the surface modulus of the fatty acid-containing solutions sharply falls down above a certain transition temperature:  $\sim 30$  °C for MAc and  $\sim 25$  °C for LAc, (Figures 1 and 3 and other unpublished data).

All these results could be explained by assuming that the molecules of the fatty acids are able to pack very well in the adsorption layers, forming a surface condensed phase (possibly a 2D molecular crystal, but this hypothesis needs verification), which renders relatively low surface tension, high surface modulus, and low tangential mobility of the surfaces. At higher temperature, this surface condensed phase melts, transforming the surfactant adsorption layer into a typical fluid layer with low surface modulus. Surface phase transitions in the adsorption layers of individual fatty acids are well documented in literature and have been studied extensively by various experimental methods.<sup>43</sup> Surface phase transitions with other types of molecules are also well-known, and have been attributed to various types of intermolecular forces in the adsorption layers.<sup>44,45</sup>

Thus we explain the role of the various components in the studied mixtures as follows: The SLES and CAPB are needed to form appropriate micelles, which are able to solubilize the molecules of the fatty acids. These micelles transport the acid molecules throughout the solution and supply them onto freshly formed solution surface. Once a sufficient concentration of LAc and MAc molecules is reached on the surface, the acid molecules



**Figure 6.** Schematic presentation of the formation of surface condensed phase of fatty acids in the adsorption layers of the studied surfactant solutions.

form surface condensed phase, thus sharply reducing the tangential surface mobility. A schematic presentation of the role of the various components and of the formation of surface condensed phase, dominated by fatty acids, is shown in Figure 6.

The envisaged simple explanation leaves a number of important questions open: Are the anionic and zwitterionic molecules incorporated inside the surface crystal or it is composed by fatty acids only? What are the types of surfactants that could provide similar behavior, besides those tested in our study? How do the surface properties depend on the pH of the solution and on solution composition (electrolyte and surfactant concentrations, presence of other surfactants, etc.)? Answering all these questions will require systematic and prolonged efforts.

#### 5. Conclusions

In the current letter we propose a new class of surfactant mixtures, which are particularly suitable for studies of foam dynamic properties. By changing the composition of these mixtures, we can vary the surface properties of the solutions and, as a result, significantly change the foam properties in dynamic processes, such as foam–wall friction, inside-foam friction, foam film thinning, Ostwald ripening, and others. These surfactant mixtures have several important advantages in comparison with other foam stabilizers that have been used for control of surface mobility so far: a wide range of surface properties is possible by varying surfactant composition, variable bulk viscosity with Newtonian behavior of the liquid phase, clear solutions without precipitates, and no gradual changes of surface properties with time (typical for proteins).

Note that, along with the surface dilatational modulus and its components discussed in this letter (Table 1 and Figure 1), there are other surface properties that might be important for foam dynamics, such as the shear surface properties (e.g., surface shear elasticity and viscosity) and the characteristic times for surfactant adsorption and desorption. Just as an example, the data for bubble Ostwald ripening in Section 3 could be explained by different characteristic desorption times of the surfactant in the various systems and/or by the different gas permeability of the adsorption layers. Therefore, the complete analysis of the role of surface properties in the various dynamic phenomena would require rather exhaustive experimental studies with respective data interpretation, which is far beyond the scope of the present study.

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